

the removal of water from hydrogen is the stream which was rejected by the membrane. However, in this current invention the stream which is treated and separated by the two membranes is the stream that permeates through the membranes, first via the most inner membrane and then via the next inner membrane. This is an additional great distinction between the two patents. Moreover, the disclosed and claimed process can utilize catalyst in more than one regions, while the Japanese process encloses catalyst only in one region as a regular fixed bed catalytic reactor. Moreover, the distinctions of the invented process from previous art including this Japanese document are summarized in a detailed manner in our Response to Office Action of 01/29/2002 mailed to USPTO on May 28, 2002. These distinctions are maintained.

The inventors based on the above, petition for the allowance and issuance of this patent application and the accompanied claims.

REMARKS SECTION

The new amended claims 134, 135, 136, 137, 152, 153, 154, 155, 170, 171, 172, 173 submitted with this amended application replace the claims of the original specification of 3/14/2000 (old claims 1-45) and the claims of the consecutive submitted specifications (old claims 1-133). Claims 138, 141, 143-151, 156-169, 174-181 drawn to inventions non-elected with traverse in the Amendment dated Nov.1, 2002 are cancelled. The inventors are requesting from USPTO to renumber the elected amended claims 134 to 173 above with the numbers from 1 to 12. Claims 134, 152, and 170 are independent claims and the remaining are dependent claims. The new claims refer to the elected and invented processes disclosed within the patent application. A clean and marked up copy of the amended claims are submitted within.

The two inventors Dr. Vasileiadis and Dr. Ziaka of this amended application are joint inventors in all disclosed amended claims submitted 134 to 172.

The new amended specification contains no new matter, is double spaced and is divided into 78 paragraphs. This new specification replaces the previous submitted

original specification. The first three reactions mentioned in the original specification have been numbered (1) to (3). In the later text of the specification, some of these numbers were misspelled and they have been corrected in the current specification and are shown in the marked up copy of the specification.

A new Oath/Declaration completed with the requested information and signed by both inventors is submitted per the Examiner's request.

The information disclosure statement has been completed with the requested information and has been mailed to the USPTO at an earlier date.

The inventors have already submitted Drawings 1 to 13 of the application in the USPTO with the original filled specification of 3/14/2000.

Amended Claims

Application number: #09/525,176

Filing Date: 03/14/2000

Inventors: Dr. Savvas Vasileiadis,
Dr. Zoe Ziaka

**“Version with markings to show changes made in
claims”
(with respect to the amended claims, Nov.1, 2002)**

Deleted Matter is shown in brackets, e.g., [membrane reactor]

Added matter is shown in bold letters e.g., **permreactor and separator**,

AMENDED CLAIMS

134. (amended) A process for conducting catalytic reforming of hydrocarbons and alcohols with steam and carbon dioxide for the production of pure hydrogen which includes:

a far outer impermeable hollow tubular cylinder nesting two more concentric permeable tubular cylinders, a next inner and a most inner one, having the most inner permeable cylinder to be nested within the next inner permeable cylinder thus defining three different annular zones including next inner membrane and most inner membrane, with the most inner permeable cylinder to be filled with a reforming catalyst and include gas heating tubes located along the most inner axis, with the catalyst to be in pellet or particle form, with the hydrogen product to be continuously removed via permeation along the most inner membrane wherein the membrane is made [by] **from** an inorganic or composite material, with the remaining reaction species to partially permeate as well via the most inner membrane, and with the permeated species to be diluted by an inert carrier gas flowing along the next inner annular zone, with hydrogen only to be continuously removed via permeation along the next inner membrane and allow for continuous hydrogen withdrawal out of the most inner catalytic zone and for continuous equilibrium shift of the reactions evolving within this zone, with next inner membrane to be made [by] **from** a metal or non-porous inorganic material permeable only to hydrogen, with the pure hydrogen to permeate through the next inner membrane and withdrawn along the far outer cylindrical zone.

135. (amended) The process of claim [1] 134 wherein the most inner membrane is made [by] **from** one or more materials selected from the group consisting of alumina, silica, titania, zirconia, yttria, and the next inner membrane made [by] **from** one or more materials selected from the group consisting of aluminum carbide and nitride, silicon carbide and nitride, titanium carbide and nitride, zirconium carbide and nitride, tantalum carbide and nitride, palladium, silver, copper, zinc, tantalum, vanadium, tungsten.

136. (amended) The process of claim [1] 134 wherein the feed hydrocarbon or alcohol is a single component or a mixture of components selected from the group consisting of methane, ethane, propane, n-butane, i-butane, methanol, ethanol, propanol, butanol, naphtha, gasoline, natural gas, coal gas [rich in] **containing** methane, landfill gas [rich in] **containing** methane, flue gas [rich in] **containing** methane, biomass and sewage gas [rich in] **containing** methane.

137. (amended) The process of claim [1] 134 wherein the combined feed hydrocarbon and carbon dioxide gas mixture is selected from the group consisting of a CH_4 and CO_2 mixture, acidic natural gas [rich in] **containing** CH_4 and CO_2 , coal gas [rich in] **containing** CH_4 and CO_2 , landfill gas [rich in] **containing** CH_4 and CO_2 , biomass and sewage gas [rich in] **containing** CH_4 and CO_2 , flue and waste gas mixture [rich in] **containing** CH_4 and CO_2 .

152. (amended) A process for conducting catalytic reforming of hydrocarbons and alcohols with steam and carbon dioxide for production of pure hydrogen which includes:

a far outer impermeable hollow tubular cylinder nesting two more concentric permeable tubular cylinders, a next-inner and a most-inner one, having the most inner permeable cylinder to be nested within the next inner permeable cylinder thus defining three different annular zones including next inner membrane and most inner membrane, with the annular space between the far outer and next-inner cylinders to be filled with a reforming catalyst, with the catalyst to be in pellet or particle form, with hydrogen to be continuously removed via permeation along the next-inner membrane wherein the membrane is made [by] from an inorganic or composite material, with the remaining reaction species to partially permeate as well via the next inner membrane, and with the permeated species to be diluted by an inert carrier gas flowing along the next inner annular zone, with hydrogen only to be continuously removed via permeation along the most inner membrane in order to allow for continuous hydrogen withdrawal out of the far outer catalytic zone and for continuous equilibrium shift of the reactions evolving within this zone, with the most inner membrane to be made [by] from a metal or non-porous inorganic material, and with the permeate pure hydrogen to be withdrawn along the most inner cylindrical zone.

153. The process of claim [19] 152 wherein the next inner membrane is made [by] from one or more materials selected from the group consisting of alumina, silica, titania, zirconia, yttria, and the most inner membrane made [by] from one or more materials selected from the group consisting of aluminum carbide and nitride, silicon carbide and nitride, titanium carbide and nitride, zirconium carbide and nitride, tantalum carbide and nitride, palladium, silver, copper, zinc, tantalum, vanadium, tungsten.

154. The process of claim [19] 152 wherein the feed hydrocarbon or alcohol is a single component or a mixture of components selected from the group consisting of methane, ethane, propane, n-butane, i-butane, methanol, ethanol, propanol, butanol, naphtha, gasoline, natural gas, coal gas [rich in] **containing** methane, landfill gas [rich in] **containing** methane, flue or waste gas [rich in] **containing** methane, biomass and sewage gas [rich in] **containing** methane.

155. The process of claim [19] 152 wherein the combined feed hydrocarbon and carbon dioxide gas mixture is selected from the group consisting of a CH_4 and CO_2 mixture, acidic natural gas [rich in] **containing** CH_4 and CO_2 , coal gas [rich in] **containing** CH_4 and CO_2 , landfill gas [rich in] **containing** CH_4 and CO_2 , biomass and sewage gas [rich in] **containing** CH_4 and CO_2 , flue and waste gas mixture [rich in] **containing** CH_4 and CO_2 .

170. A process for conducting catalytic hydrocarbon reforming with carbon dioxide, for production of pure hydrogen and carbon dioxide which includes:

a far outer impermeable hollow tubular cylinder nesting two more concentric permeable tubular cylinders, a next-inner and a most-inner one, having the most inner permeable cylinder to be nested within the next inner permeable cylinder thus defining three different annular zones including next inner membrane and most inner membrane, with the annular space between the far outer and next-inner cylinders to be filled with a reforming catalyst in pellet or particle form, with hydrogen and carbon dioxide to be

continuously removed via permeation along the next-inner membrane wherein the membrane is made [by] from an inorganic or composite material, with the remaining reaction species to partially permeate as well via the next inner membrane and with the permeated species to be diluted by an inert carrier gas flowing along the next inner annular zone, with hydrogen and carbon dioxide species to be continuously removed via permeation along the most inner membrane, with the most inner membrane to be made [by] from a polymer or inorganic material which is permeable to both hydrogen and carbon dioxide species, with the permeated binary hydrogen-carbon dioxide mixture to be withdrawn by flowing along the most inner cylindrical zone.

171. The process of claim [37] 170 wherein the next inner membrane is made [by] from one or more materials selected from the group consisting of alumina, silica, titania, zirconia, yttria, and the most inner membrane made [by] from one or more materials selected from the group consisting of alumina, silica, titania, zirconia, yttria, polyimides, polycarbonates, polybenzimidazoles, polyphosphazenes, polysulfones.

172. The process of claim [37] 170 wherein the feed hydrocarbon or alcohol is a single component or a mixture of components selected from the group consisting of methane, ethane, propane, n-butane, i-butane, methanol, ethanol, propanol, butanol, naphtha, gasoline, natural gas, coal gas [rich in] containing methane, landfill gas [rich in] containing methane, flue and waste gas [rich in] containing methane, biomass and sewage gas [rich in] containing methane.

173. The process of claim [37] 170 wherein the combined feed hydrocarbon and carbon dioxide gas mixture is selected from the group consisting of a CH_4 and CO_2 mixture, acidic natural gas [rich in] containing CH_4 and CO_2 , coal gas [rich in] containing CH_4 and CO_2 , landfill gas [rich in] containing CH_4 and CO_2 , biomass and sewage gas [rich in] containing CH_4 and CO_2 , flue and waste gas mixtures [rich in] containing CH_4 and CO_2 .

part of paper # 22

Application number: #09/525,176

Filing Date: 03/14/2000

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**"Version with markings to show changes made"
with respect to the pages of the original
specification, 3/14/2000)**

Deleted Matter is shown in brackets,

e.g., [membrane reactor]

Added matter is shown in bold letters,

e.g., **permreactor and
separator,**

impermeable metal shell which is interconnected with all the membrane tubes and sealed from the gases flowing into the catalytic reaction side (3). Optionally, a flowing component can flow along the inner membrane tube (1) to sweep and dilute the permeate gas as it flows through the tubes.

36 In an optional design, catalyst in form of pellets or particles (4) can be contained within the inner side of the polymer membrane tubes to carry suitable catalytic reactions (such as hydrogenations) in which one of the reacting species is permeate hydrogen and the other reaction species are contained within the flowing gas. Such a flowing (sweep) component can be an unsaturated hydrocarbon (e.g., alkenes, alkynes) for conversion to saturated hydrocarbons, after reaction with hydrogen, in an exothermic reaction. Flowing (sweep) component can also be carbon monoxide for direct production of methanol or gasoline (through Fischer-Tropsch synthesis) after combination with the permeate hydrogen, in exothermic type reactions. Flowing gas can be nitrogen for exothermic ammonia synthesis after its combination with the permeate hydrogen. Other combination reactions with permeate hydrogen over specific metallic catalysts, can be these for reduction of aromatic hydrocarbons, also these for saturation of unsaturated alcohols, phenols, aldehydes, ketones, acids, these for reduction of alkyl and aryl halides and these for reduction of nitroalkanes and aromatic nitro compounds to corresponding primary amines. Part of the heat generated by the exothermic reactions in the inner side of the tubes, may be transferred across the membranes, into the common catalytic reaction zone (3) surrounding the multiple membrane tubes, thus providing part of the heat load necessary to drive the endothermic catalytic reactions in catalyst zone (3).

ammonia synthesis. Other combination (synthesis) reactions with permeate hydrogen can be these for reduction of aromatic hydrocarbons, also these for saturation of unsaturated alcohols, phenols, aldehydes, ketones, acids, these for reduction of alkyl and aryl halides and these for reduction of nitroalkanes and aromatic nitro compounds to corresponding primary amines.

48 The described process is able to overcome the thermodynamic equilibrium limitations of hydrocarbon (CH_4) and CO_2 reactant conversion, through the removal of H_2 only, or of H_2 and CO_2 gases in membrane permreactor A and permeator D. The calorific value of the obtained H_2 , CO product in permreactor A, is higher than this of the reactant hydrocarbon (e.g., CH_4), CO_2 and steam and the endothermic heat of reaction is stored in the products which can be subsequently used as fuels or in chemical synthesis.

49 Assuming 100% conversion of reactions (1) and [(3)] (2), and reaction (3) in equilibrium in permreactor A, 2 mol of CH_4 (with heat of combustion: 425.6 kcal), 1 mol of CO_2 (with no heat of combustion), and 1 mol of $\text{H}_2\text{O}(\text{g})$ (with no heat of combustion), produce 3 mol of CO (with heat of combustion: 202.8 kcal) and 5 mol of H_2 (with heat of combustion: 341.5 kcal). These values are at 25°C . This corresponds to about 28% increase in calorific value for the product. Endothermic heat can be provided in reformers A and B through the combustion of flue or waste gases or unreacted recycled hydrocarbons coming out of the exit of reaction zone of reformers A and B as also described in Figs.1 and 3 above.

50 In an alternative design, permeator D is replaced by a catalytic permreactor D wherein the water gas shift reaction occurs if stream 8 is rich in product CO. In such case permreactor D is made by metal, non-porous inorganic, or carbon membranes to separate

can be provided in dehydrogenator A through the combustion of flue or waste hydrocarbons or unreacted recycled hydrocarbons from the reaction zone of reactor A as also described in embodiments of Figs. 1, 3 and 5 above.

61 Permeable dehydrogenator A can be substituted by non-permeable (e.g., non-porous stainless steel wall) dehydrogenator A. Valve A1 and stream 1b are eliminated and all post-reaction gases exit from stream 2. Permeator C still operates in same function as described above.

62 Fig. 9, is an embodiment which is related with these described in Figs. 6 and 7, but with stream 1 to contain hydrocarbon feedstocks such as methane or higher alkanes such as naphtha and natural gas, also alcohol feedstocks such as methanol, ethanol, propanol, butanol mixed with steam only and introduced in catalytic permreactor A which is filled with catalyst particles to conduct the methane steam reforming reaction (1) and the simultaneously occurring water gas shift reaction [(2)] (3). Some hydrogen may be added into stream 1, which is usually between 1-15% of the feed volume, to depress carbon formation from hydrocarbon cracking especially in the inlet of the reactor A.

63 Catalytic permeable reformer A, is of any of the types described in embodiments of Figs. 1, 2, 3, 4, and 5 above, with H_2 to be separated in permeate stream 1b via valve A1, in the general case. H_2 and CO_2 combined, can be separated in permeate stream in special applications, if an organic membrane is used in permreactor A. The rejected exit stream from the permreactor may contain product CO_2 , CO, unreacted steam ($H_2O(g)$) and hydrocarbon, and non-permeate H_2 . This stream becomes stream 2 and enters into heat exchanger B, where the unreacted steam is removed through condensation, and by the heat exchanging process new steam is generated in stream 8 from the water or steam of

stream 7. Stream 8, can provide steam in permreactor A and reactor E through streams 6 and 10,20 respectively, in an alternative or simultaneous manner via use of valves B1,E1. The steam in 8 acquires the exchanged heat load from stream 2, the hot gas effluent from permeable reformer A, and thus its derived streams 6,10,20 can be mixed directly with streams 1 and 14 which are fed directly into reactors A and E respectively.

64 Steam from 8 is used via streams 10,20 and valve E1 to provide initial steam in reformer E. Stream 9 passes through a bed of particles (moisture adsorbent) C to remove any non-condensed traces of moisture and through exit stream 11 enters into membrane permeator D. Stream 11 has been cooled in temperature of permeator D and contains CO, CO₂, unreacted hydrocarbon, non-permeate H₂ gas species.

65 H₂ or both H₂ and CO₂ are removed in permeate stream 12 of permeator D. through the permselective action of a metal, non-porous inorganic, carbon or organic membrane respectively. Non permeating stream containing hydrocarbon (e.g., CH₄), CO and CO₂ or hydrocarbon and CO respectively, depending on the type of membrane used in permeator D, exits from permeator D, through stream 13 as reject stream. In case wherein stream 13 contains hydrocarbon and CO it can be recycled via valve D1 and stream 5 into first permeable reformer A for continuous reforming and conversion to main H₂ and CO₂ products. Alternatively, by use of valve D1, stream 13 becomes stream 14 which enters into steam reformer E for additional reforming and shift reactions, via reactions (1) and ([2]) (3) and additional conversion to H₂ and CO₂ products. In case wherein stream 13 contains hydrocarbon, CO and CO₂, using valve D1, stream 13 becomes stream 14 which enters into modified steam and CO₂ reformer E for additional

provided endothermic heat of reaction is stored in the products and can be subsequently released by using products as fuels or in chemical synthesis.

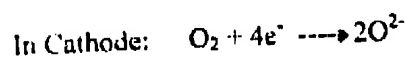
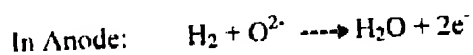
(v) Assuming 100% conversion of reactions (1) and (2) (3), 1 mol of CH_4 (with heat of combustion: 212.8 kcal) and 2 mol of $\text{H}_2\text{O}(\text{g})$ (with no heat of combustion) generate 1 mol of CO_2 (with no heat of combustion) and 4 mol of H_2 (with heat of combustion:

273.4 kcal). These values are at 25°C . This corresponds to about 28% increase in calorific value for the product gases. By providing external heat through flue or waste gas input in the reformers and with the described two heat exchangers in place, the energy requirement of the one reactor-one permeator or two reactor-one permeator cascades is fulfilled and the processes operates in a thermally independent manner providing for an energy efficient design. Endothermic heat can be provided in reformers A and E through the combustion of flue or waste gases or unreacted recycled hydrocarbons from the reaction zone of reformers A and E, as also described in Figs.1,3,5 above.

70 Fig.10. is an embodiment of a steam and CO_2 hydrocarbon reforming process which includes a permeable reformer or a non-permeable reformer followed by a cryogenic separator for separation of certain post-reaction gases exiting from the reject exit of the reformer. In Fig.10, stream 1 is introduced into catalytic permreactor A, containing hydrocarbon feedstocks such as methane (CH_4) mixed with steam and CO_2 for conducting simultaneously reactions (1), (2) and (3), or mixed with CO_2 only for conducting reactions (2) and (3). Some hydrogen may be added into stream 1, which is usually between 1-15% of the feed volume, to depress carbon formation from methane cracking especially in the inlet of permreactor A.

eliminated and all product H_2 is included in post-reaction mixture entering through stream 2 into cryogenic separator B.

73 Fig.11, is a modified embodiment of the process described in Fig.6. It applies to complete conversion of hydrocarbon (i.e., CH_4) and CO_2 reactants of stream 1, within the permeable reformer A, to H_2 and CO products. The occurring reactions are (1),(2),(3) or (2),(3) only. Catalytic permeable reformer A, is of any of the types described in embodiments of Figs. 1,2,3,4, and 5 above, with H_2 to be separated in permeate stream 3 via valve A1. Exiting from the permeator, stream 2, containing only CO and non-permeating H_2 , or CO, non-permeating H_2 , and traces of unreacted steam, enters into a solid oxide fuel cell (SOFC) unit B. Stream 2 is directed in the anode of the solid oxide cell, and consists the fuel constituent of the fuel cell. O_2 in stream 4, is directed in the cathode of the fuel cell and [consist] consists the oxidant, for the well known electrochemical reaction conducted within the cell with electric current generation:



Optionally, part of hydrogen from permeate stream 3, can be fed into stream 2, via bypass stream 3b, to adjust the composition of H_2 in stream 2 to that required to feed the fuel cell B. The reformer A can be optionally substituted by a non-permeable reformer A, wherein all product H_2 is included in exit stream 2. Flue gas streams 5 and 6, are used to provide the endothermic heat content into the reformer A. Stream 5 can be fed by a bypass stream of exit stream 2, as also described in embodiments of Figs.1,3,5. Permeable reformer A can be substituted by a non-permeable (e.g., stainless steel) reformer A. Valve A1

[stream] streams 3, 3b are eliminated and all post-reaction gases exit from stream 2. Fuel cell B still operates in same function as described above.

74 Fig.12. is an embodiment which describes a modified operation of the process described in Fig.6. It applies to complete conversion of hydrocarbon (i.e., CH_4) and CO_2 reactants of stream 1, within the permeable reformer A, to H_2 and CO products. The occurring reactions within the reformer are (1),(2),(3) or (2),(3) only. Catalytic permeable reformer A, is of any of the types described in embodiments of Figs. 1,2,3,4, and 5 above, with H_2 to be separated in permeate stream 1b via valve A1. Exiting from the permeator, stream 2, containing only CO and non-permeating H_2 , or CO , non-permeating H_2 , and traces of unreacted steam, passes through heat exchanger B and moisture adsorbent C to remove unreacted steam, and enters into permeator D as a dry stream. Hydrogen is separated in stream 11 from carbon monoxide, rejected by the membrane, and exiting via stream 12. Carbon monoxide, via stream 12, can be optionally fed into a consecutive water gas shift reactor E for conversion to final H_2 and CO_2 products. A heat exchanger F is used in exit of the water gas shift reactor E, to remove any unreacted steam, with final stream 15 to contain only H_2 and CO_2 . The reformer A can be optionally substituted by a non-permeable reformer A, wherein all reaction product H_2 is included in exit stream 2 and stream 1b, valve A1 are eliminated.

75 Hydrogen from stream 11 can be used in applications mentioned already in embodiment described in Fig.6 and Fig.9. Similarly CO from stream 12, or H_2 and CO_2 from stream 15 can be used in aforementioned applications described already in embodiments of Figs. 6,9 and 10.

stream 14 is H_2 and CO_2 . Steam in reactor E is provided through streams 6, 10, 13, [(20)] 15 which is generated by the heat exchanging process in heat exchangers B and F.

77 Pure H_2 and CO_2 mixture from exit stream 14, can be used as feed in molten carbonate fuel cells or in alternative methanol synthesis via the opposite reaction of methanol steam reforming, listed above. Optionally, bypass stream 16 can be fed into stream 8 to add CO_2 and H_2 into the synthesis gas mixture fed into reactor D, to adjust its composition for increasing methanol production efficiency in the catalyst in reactor D via the reverse (13.2) reaction. Optionally also, stream 1c, which is a bypass stream of stream 1b and contains pure hydrogen, can be recycled into stream 8 via stream 16, for adjusting the hydrogen composition in this stream where necessary, to increase the efficiency of methanol synthesis in reactor D. Streams 15 and 1c merge into stream 16 via valve D1.

78 Hydrogen in stream 14 can be used as a mixture with CO_2 , or as pure H_2 after the CO_2 condensation and removal. Produced hydrogen from streams 1b and 14, can be used in applications mentioned already in embodiments described in Fig.6 and Fig.9. The H_2 and CO_2 mixture of stream 14 can be used in synthesis or fuel applications mentioned already in same embodiments. Reformers A and E are endothermic and flue gas streams 3, 4 and 18, 19 respectively are used to provide the necessary heat content to drive parallel reactions (1), (2), (3) and (13.2) respectively to completion. Streams 3 and 18 can be fed by a bypass stream of stream 2. Optionally, reformer A can be a non-permeable reformer with only one post-reaction outlet (exit), this of stream 2, which delivers all products and unreacted reactants into the heat exchanger B and next into reactor D.